CONDUCTIVE LIQUID CRYSTAL DEVICE

AND ORGANIC ELECTROLUMINESCENCE DEVICE

FIELD OF THE INVENTION AND RELATED ART

5   The present invention relates to an electroconductive liquid crystal device, particularly a conductive liquid crystal device useful as an organic electroluminescence device (hereinafter, the term "electroluminescence" being sometimes abbreviated 10 as "EL" according to common usage in the field).

As for the organic EL device, carrier injection-type EL devices utilizing organic solids, such as anthracene single crystal, were studied in detail in years of 1960's. These devices were of a 15 single layer-type, but thereafter Tang, et al proposed a lamination-type organic EL device comprising a luminescence layer and a hole transporting layer between a hole injecting electrode and an electron injecting electrode. The luminescence mechanism in 20 these injection-type EL devices commonly includes stages of (1) electron injection from a cathode and hole injection from an anode, (2) movement of electrons and holes within a solid, (3) re-combination of electrons and holes, and (4) luminescence from the 25 resultant single term excitons.

A representative example of the lamination-type EL device may have a structure including an ITO

film as a cathode formed on a glass substrate, a ca. 50 nm-thick layer formed thereon of TPD (N,N'-diphenyl-N,N'-di(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine), a ca. 50 nm-thick layer thereon of Alq3

5 (tris(8-quinolinolato)-aluminum), and further a vacuum deposition layer of Al-Li alloy as a cathode. By setting the work function of the ITO used as the anode at 4.4 - 5.0 eV, the hole injection to TPD is made easier, and the cathode is composed of a metal which

10 has as small a work function as possible and also is stable. Examples of the cathode metal may include Al-Li alloy as mentioned above and also Mg-Ag alloy. By the above organization, green luminescence may be obtained by applying a DC voltage of 5 - 10 volts.

15 An example using a conductive liquid crystal as a carrier transporting layer is also known. For example, D. Adam et al (Nature, Vol. 371, p. 141-) have reported that a long-chain triphenylene compound as a discotic liquid crystal material exhibited a

20 mobility of 10^{-3} - 10^{-2} cm^2/V.sec in its liquid crystal phase (Dh phase) and a mobility of 10^{-1} cm^2/V.sec in its mesophase (an intermediate phase, not a liquid crystal phase). Also, as for a bar-shaped liquid crystal, Junichi Hanna (Ohyou Butsuri

25 (Applied Physics), Vol. 68, No. 1, p. 26-) has reported that a phenylnaphthalene compound exhibited a mobility of 10^{-3} cm^2/V.sec or higher in its smectic

B phase.

As a trial for using such a liquid crystal for electroluminescence, INGAH STAPFF et al. (Liquid Crystals, Vol. 23, No. 4, pp. 613-617) have reported an organic EL device using a triphenylene-type discotic liquid crystal. Other reports are found in POLYMERS FOR ADVANCES TECHNOLOGIES, Vol. 9, pp. 463-460 (1998), and ADVANCED MATERIALS (1997), Vol. 9, No. 1, p. 48-.

Convention organic EL devices have involved several problems attributable to the use of a low-molecular weight compound in a crystal state. A first problem is that the efficiency of injection of electrons or holes from electrodes of ITO, etc., to the organic layers is low. This is because minute grain boundary in a crystal state of organic molecules functions as a carrier conduction barrier. Accordingly, organic molecules in an amorphous state are generally used though it incurs a low carrier injection efficiency. This however has provided a major cause why an organic EL device cannot ensure a large current.

An organic material used in an organic EL device has an electronic structure providing a large energy gap of ca. 3 eV or larger, thermal excitation-type free electrons are not present in a conduction band, a drive current (spatial charge restriction

current) is principally supplied by injected carriers from the electrodes, so that a low carrier injection efficiency from the electrodes has been a serious problem. As the injection efficiency is low, a large voltage has to be applied in order to ensure a drive current, and the device layer thickness has to be lowered. These factors have caused difficulties, such as a short circuit between the electrodes and an increase in capacitive load.

As a second problem, an organic EL device is liable to be affected by invaded moisture to cause deterioration of luminescence performance and drive performance, thus showing poor durability. In an ordinary organic EL device, the organic layers are disposed in lamination and then the cathode is formed thereon by vapor deposition of a metal film. In this instance, a metal species having a small work function suitable for the cathode is susceptible of oxidation and has a low durability. Even in case of forming a protective film thereon by sputtering, the organic layers are liable to be degraded if the forming temperature is high (with an ordinary limit of 100 ^{o}C), and the destruction of the device structure due to the film stress is also problematic.

On the other hand, as a problem accompanying the use of a conducive liquid crystal for constituting a carrier transporting layer, it is difficult to align

a high order liquid crystal layer. As a high order
conductivity can be attained by a regular stacking of
π-electron conjugated planes of liquid crystal
molecules, the degree of alignment thereof directly

5 affects the conductivity of the resultant conductive
liquid crystal layer. In the case case of a poor
alignment characteristic, trap sites for conduction of
electrons and holes can be formed in the liquid
crystal layer, so that electroconductivity can be lost

10 at all in some cases.

SUMMARY OF THE INVENTION

A generic object of the present invention is
to provide an improvement to the above-mentioned state

15 of art.

A more specific object of the present
invention is to provide a conductive liquid crystal
device including a conductive liquid crystal layer
having locally different regions by controlling

20 partially or entirely controlling the alignment state
of a conductive liquid crystalline organic layer
formed on an electrode.

Another object of the present invention is to
provide a conductive liquid crystal device wherein

25 such a conductive liquid crystal layer is provided
with locally different conductivities and a memory
characteristic, thereby causing luminescence

exhibiting different luminances at an identical drive voltage.

According to another aspect of the present invention, there is provided an organic

5   electroluminescence device comprising: a conductive liquid crystal device which includes a pair of oppositely disposed electrodes and a liquid crystalline organic layer disposed between the electrodes, wherein the organic layer has plural

10   regions having mutually different alignment states resulting in different luminances of luminescence from the device.

The present invention further provides an organic electroluminescence device comprising: a

15   conductive liquid crystal device which includes a pair of oppositely disposed electrodes and at least two organic layers disposed between the electrodes, wherein said at least two organic layers include at least one liquid crystalline organic layer having

20   plural regions of different electroconductivities resulting in different luminances of luminescence from the device.

These and other objects, features and advantages of the present invention will become more

25   apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the

accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic sectional view of an embodiment of the conductive liquid crystal device according to the invention.

Figure 2A is a schematic sectional view of an organic EL device according to Example 1 of the invention, and Figure 2B is a corresponding bottom plan view.

Figure 3 is a schematic sectional view of an organic EL device according to Example 2 of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to an embodiment, the conductive liquid crystal device of the present invention may be produced by forming a conductive liquid crystalline organic layer on an electrode, and controlling an alignment state of the conductive liquid crystalline organic layer locally or entirely to form regions of mutually different electroconductivities, leading to different luminances of luminescence when used as an organic EL device.

A high electric field on the order of 10 volts/100 nm has been required for the drive of an organic EL device because of (1) a low mobility of

carriers (holes an electrons) through organic layers and (2) a low efficiency of injection of carriers into the organic layers from the electrodes. Organic materials used in organic EL devices have a broad band gap of ca. 3.0 eV, so that thermal excitation-type free electrons are not present in a conduction band (LUMO: lowest unoccupied molecular orbital), and drive current is principally supplied by a tunnel current injected from the electrodes. The injection efficiency of the current is known to be remarkably affected not only by the work functions of the electrodes and a level gap between LUMO and HOMO (Highest Occupied Molecular Orbital) of the organic materials but also by the molecular alignment and structure of the organic materials. However, in order to attain a sufficient drive current by using ordinary organic compounds (such as TPD, α-NPD (bis[N-(1-naphthyl)-N-phenyl]benzidine), TAZ-01 (3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole), Alq3, etc.) in ordinary EL devices, it has been necessary to apply a high electric field (on the order of 10 V/100 nm) across the organic layer-electrode boundaries. Further, as the mobility of the organic materials is on the order of 10^{-6} - 10^{-3} cm^2/V.sec, it is also necessary to apply a high electric field in order to ensure a drive current. Some improvement to the above problem has been given by using a conductive liquid

crystal for constituting a liquid crystalline charge injection layer as proposed by our research group (EP-A 1083613 and EP-A 1089596).

The use of a conductive liquid crystal for constituting a charge injection layer is effective because of the following reasons and functions.

(1)   Some conductive liquid crystallines have a mobility exceeding 10^{-2} cm^2/V.sec (D. Adam, et al; Nature Vol. 371, p. 141-).

(2)   A conductive liquid crystal causes a phase transition at a higher temperature to assume a lower order liquid crystal phase, such as nematic phase or discotic disordered phase, thereby showing a good alignment characteristic to cause alignment of liquid crystal molecules over an electrode surface.

(3)   Especially, a discotic liquid crystal generally has a structure including a core of, e.g., triphenylene, and side chains attached to the periphery of the core for developing mesomorphism (liquid crystal property). The side chains generally exhibit poor wettability with a substrate of a metal or a metal oxide (such as ITO), so that in the liquid crystal state of the discotic liquid crystal, the core is aligned parallel to the electrode surface, whereby the π-electron resonance plane of the core is aligned parallel to the electrode surface, thereby facilitating carrier transfer with the electrode.

Accordingly, it is possible to provide a higher injection efficiency than an ordinary organic compound in an amorphous state.

This effect can also expected for an ordinary bar-shaped liquid crystal having a molecular structure including a phenyl group or a naphthalene group having a π-electron resonance plane.

(4) The formation of a conductive liquid crystal layer as a carrier transporting layer by vacuum deposition is particularly effective. A liquid crystal film layer formed by vacuum deposition has a coarse molecular packing state, the re-alignment thereof by heating is very easy. This is particularly true with a liquid crystal film formed by vacuum deposition on a substrate at a temperature close to or below Tg (glass transition temperature) of the liquid crystal giving a stably coarse film structure.

(5) A high-order liquid crystal phase having a higher degree of order has a low fluidity; and the alignment thereof in the high-order liquid crystal phase per se is difficult, whereas the alignment characteristic thereof can be improved if the liquid crystal layer is sandwiched between films having a power of aligning π-electron conjugated planes parallel thereto. Realignment by heating up to the isotropic phase is not desirable for device formation sometimes because of a strong dissolving power of the

liquid crystal material in a liquid phase to other organic materials, but the dissolution problem is not encountered at a boundary with a metal film. In the case of sandwiching a liquid crystal with metal films,

5   one of them is required to allow light-transmission. For example, in the case of using a gold film, the film may be formed as an island-like uneven film, but the alignment thereby of a liquid crystal can be improved than in the absence of such a gold film.

10   (6) A molecule exhibiting mesomorphism can re-organize molecular disposition at the electrode surface by re-aligning post treatment. This can facilitate the injection efficiency. The post treatment can exhibit a large effect even when it is

15   performed by heating only to a liquid crystal phase temperature if it provides a lower viscosity. The heating to the isotropic temperature, while it is effective for the re-alignment, has to be suppressed to a temperature below the Tg of other organic

20   materials used together therewith.

       (7) At a boundary of a luminescence layer with a liquid crystal layer or an intermediate metal layer, it is effective to insert a protective layer comprising a material having a function of

25   transporting a carrier of the same type.

       In the present invention, such a conductive liquid crystal layer is formed while noting the above

points, so as to provide regions of different
electroconductivities by locally changing the
alignment state thereof.

The local alignment state change is
5   principally performed by local heating of the
conductive liquid crystalline organic layer. This can
alternatively be effected by a surface treatment of an
electrode surfaces, such as local surface roughening
at regions for not aligning the liquid crystal on the
10 electrode surface.

The conductive liquid crystal device
structure including a conductive liquid crystal layer
having a locally different conductivity can be
effectively used for constituting an organic EL device
15 as described in detail below but also for constituting
other functional devices, such as a photosensor, a
photoconductor (electrophotographic photosensitive
member), an organic semiconductor device (such as an
organic TFT), a temperature sensor, and a space
20 modulation device.

Figure 1 is a schematic sectional view of an
embodiment of the conductive liquid crystal device
according to the present invention. Referring to
Figure 1, the conductive liquid crystal device
25 includes a transparent substrate 1, and a transparent
electrode (anode) 2, a liquid crystalline organic
layer 3, a luminescence layer 5 and a metal electrode

(cathode) 6 disposed in this order on the substrate 1,
wherein the liquid crystalline organic layer 3 is
provided with plural regions having mutually different
electroconductivities including non-aligned liquid
crystal regions 3a having a lower conductivity and
aligned liquid crystal regions 3b having a higher
conductivity.

The liquid crystalline organic layer 3
comprises a liquid crystalline or mesomorphic compound
having a liquid crystal phase at some temperature,
inclusive of low-molecular weight (non-polymeric)
conductive liquid crystals and polymeric conductive
liquid crystals. The conductive liquid crystal may
suitably have a π-electron resonance structure, which
is generally given by an aromatic ring. Examples
thereof may include: triphenylene ring, naphthalene
ring and benzene ring, as representative, and also
pyridine ring, pyrimidine ring, pyridazine ring,
pyrazine ring, tropone ring, azulene ring, benzofuran
ring, indole ring, indazole ring, benzothiazole ring,
benzoxazole ring, benzimidazole ring, quinoline ring,
isoquinoline ring, quinazoline ring, quinoxaline ring,
phenanthrene ring and anthracene ring.

The conductive liquid crystal used in the
present invention may preferably comprise a discotic
liquid crystal or a smectic liquid crystal. A
discotic liquid crystal may generally have a core

structure which may be given by an aromatic ring as mentioned above for the π-electron resonance structure, as represented by triphenylene ring (or skeleton). Further examples thereof may include

5 truxene skeleton, metal-phthalocyanine skeleton, phthalocyanine skeleton, dibenzopyrene skeleton, metal-naphthalocyanine skeleton, dibenzopyrene skeleton, and hexabenzocoronene skeleton.

As for the electrode materials used in the

10 present invention, examples of material constituting the anode 2 may include: indium oxide, tin oxide, Cd_2SnO_4, zinc oxide, copper iodide, gold and platinum, in addition to ITO used in Examples described hereinafter. Examples of material constituting the

15 cathode 6 may include: alkali metals, alkaline earth metals and alloys of these, inclusive of sodium, potassium, magnesium, lithium, sodium-potassium alloy, magnesium-indium alloy, magnesium-silver alloy, aluminum, aluminum-lithium alloy, aluminum-copper

20 alloy, aluminum-copper-silicon alloy.

Further, examples of materials for the luminescence layer 5 may include: in addition to Alq3, BeBq (bis(benzoquinolinolato)beryllium), DTVB2 (4,4'-bis(2,2-di-p-tolylvinyl)biphenyl), Eu(DBM)3(Phen)

25 (tris(1,3-diphenyl-1,3-propanediono)-monophenanthroline)Eu(III)), and further, diphenyl-ethylene derivatives, triphenylamine derivatives,

diaminocarbazole derivatives, bisstyryl derivatives, benzothiazole derivatives, benzoxazole derivatives, aromatic diamine derivatives, quinacridone compounds, perylene compounds, oxadiazole derivatives, coumarin compounds, anthraquinone derivatives, distyrylarylene derivatives (DPVBi), and oligothiophene derivatives (BMA-3T).

Further, as mentioned above, a protective layer can be inserted adjacent to the liquid crystalline organic layer 3. The protective layer may preferably comprise a material having a large volume so as to exhibit little diffusivity into liquid crystalline materials used in the liquid crystalline organic layer 3. It is further preferred that the protective layer material does not have a liquid crystal phase of an order equivalent to or lower than that of a disordered phase at an operation temperature, and more preferably is a non-liquid crystal material. Examples thereof may include:

α-NPD: bis[N-1-(naphthyl)-N-phenyl]benzidine,

1-TANTA: 4,4',4"-tris(1-naphthylphenylamino)-triphenylamine,

2-TANTA: 4,4',4"-tris(2-naphthylphenylamino)-triphenylamine,

TCTA: 4,4',4"-tris(N-carbazoyl)triphenylamine,

p-DPA-TDAB: 1,3,5-tris[N-(4-diphenylaminophenyl)-phenylamino]benzene,

TDAB: 1,3,5-tris(diphenylamino)benzene,

DTATA: 4,4',4"-tris(diphenylamino)triphenylamine,

TDAPB: 1,3,5-tris[(diphenylamino)phenyl]benzene.

[Examples]

5   Hereinbelow, the present invention will be described more specifically based on Examples.

(Example 1)

An organic EL device having a sectional structure as shown in Figure 2A (which is

10   substantially identical to Figure 1) which is a sectional view taken along a line A-A' in Figure 2B, a corresponding bottom plan view, was prepared in the following manner.

More specifically, on a glass substrate 11

15   held at 200 $^\circ$C, a 70 nm-thick ITO film was formed as a hole-injecting anode 12 by sputtering using a target of In 90 wt. % and Sn 10 wt. % while flowing Ar gas at 200 sccm and O_2 gas at 3 sccm. The ITO film showed a work function of ca. 4.35 eV after the sputtering but

20   was then exposed to ultraviolet rays from a low-pressure mercury lamp to have an elevated work function of ca. 4.6 eV.

The above-treated glass substrate 11 having an ITO film 12 was placed in a vacuum chamber held at

25   a pressure below 2.67 x 10^{-3} Pa (2x10^{-5} torr), and a ca. 35 nm-thick layer of HHOT (hexabis(hexyloxy)-triphenylene) of a formula shown below was formed as a

conductive liquid crystal layer 13 on the ITO film 12

by vacuum deposition at a rate of ca. 0.1 nm/sec at a

pressure of 1.33×10^{-3} Pa (1×10^{-5} torr) according to

the resistance heating vacuum deposition method. HHOT

5   exhibited a mobility of 1×10^{-3} cm^2/V.sec at ca. 70 ^{O}C

or below according to the time-of-flight method.

Incidentally, HHOT is a discotic liquid crystal

causing a transition from crystal to discotic

disordered phase at 65 ^{O}C and a transition to

10   isotropic phase at 98 ^{O}C.

15

HHOT

R = $C_6H_{13}O$

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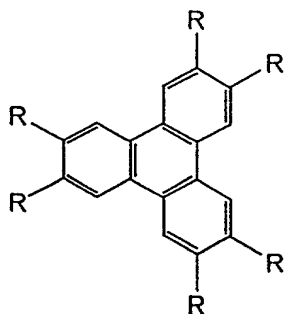
Then, on the HHOT layer 13, a luminescence
layer 15 of Alq_3 represented by a structural formula
shown below was formed in a thickness of 60 nm by
vacuum deposition at a rate of ca. 0.1 nm/sec under a
5   pressure of 1.33×10^{-3} Pa (1×10^{-5} torr).

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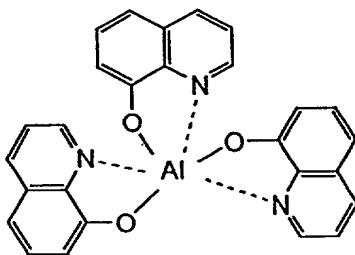
Then, the Alq_3 layer 15 was further coated
with a cathode metal 16 comprising a 50 nm-thick layer
of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm
15   thick Al layer, respectively formed by vacuum
deposition, to form a device structure roughly as
shown in Figure 2A.

In this state, all the organic layers 13 and
15 were in an amorphous (non-aligned) state. In this
20   state, the liquid crystal layer 13 was locally
irradiated with GaAlAs laser beam (beam diameter = ca.
20 μm, 10 mW) and cooled by standing to be provided
with locally aligned portions 13b showing a higher
conductivity than non-irradiated, non-aligned regions
25   13a.

As a result, an organic EL device having a
sectional structure as shown in Figure 2A was

obtained.

The organic EL device was subjected to voltage application under an electric field of 12 volts/100 nm. As a result, the device exhibited

5   luminescence with different luminescences at laser-irradiated parts 13b and non-irradiated parts 13a as shown in Table 1 below and exhibited a display state as shown i Figure 2B giving a sufficient contrast between the irradiated luminescent parts 17 and non-

10   irradiated non-luminescent parts 18.

Table 1

|	Current (mA/cm^2)	Luminance (cd/m^2)
Laser-irradiated aligned parts	3.593	120
Non-irradiated non-aligned parts	0.05	1.5

20

(Example 2)

An organic EL device having a sectional structure as shown in Figure 3 including a pixel structure and a conductive liquid crystal layer 53

25   having a higher conductivity region 53b corresponding to a selected pixel formed by high voltage application was prepared in the following manner.

A glass substrate 51 coated with a 70 nm-thick ITO layer (anode) 52 and a ca. 35 nm-thick HHOT layer (conductive liquid crystal layer) 53 was prepared in the same manner as in Example 1.

5   Then, on the HHOT layer 53, a protective layer 54 of αNPD represented by a structural formula shown below was formed in a thickness of 60 nm by vacuum deposition at a rate of ca. 0.1 nm/sec under a pressure of 1.33×10^{-3} Pa.

10

α-N P D

15
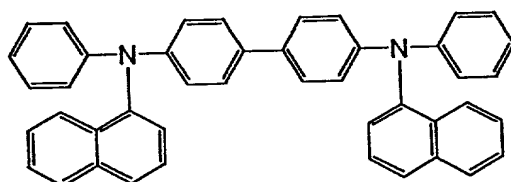
Luminescence organic layer segments 55a – 55c exhibiting different luminescent wavelengths were respectively formed in a thickness of 50 nm on the protective layer 54 by vacuum deposition through a

20   mask under the conditions of a pressure of 1×10^{-5} torr and a deposition rate of ca. 0.1 nm/sec. The organic layers 55a – 55c were respectively formed of Alq3 alone, Alq3 doped with 5 wt. % of perylene for shifting the luminescence wavelength to a shorter

25   wavelength side, and Alq3 doped with 5 wt. % of DCM (a styryl dye) for shifting to a longer wavelength side. The structural formulae for the above-mentioned

perylene and DCM are shown below.

perylene

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DCM

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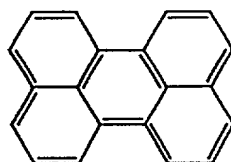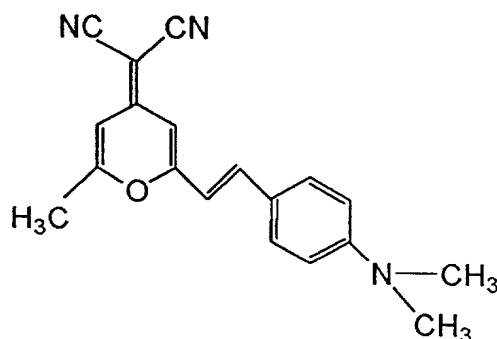
The above-prepared organic layers 55a - 55c were respectively coated with cathode metals 56 each comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm-thick Al layer,

20 respectively formed by vacuum deposition, to obtain an organic EL device having a structure as shown in Figure 3.

The above-prepared device was confirmed to exhibit luminescence of respective colors at segments

25 55a - 55c at an increased luminance at an increased current when maintained at 75 $^{\circ}$C.

In this example, only a selected pixel

portion of the organic layers including a luminescence segment (55a in Figure 3) was supplied with a high electric field of 15 volts/100 nm for 3 min. at 30 ^{O}C, and the other segments (55b and 55c in Figure 3) were not subjected to the high voltage application treatment. Thereafter, all the segments 55a - 55c were supplied with a drive electric field of 5 volts/100 nm at 30 ^{O}C. As a result, the segment 55c subjected to the high-voltage application treatment exhibited a selectively high luminance as shown in Table 2 below.

Table 2

	Current (mA/cm^2)	Luminance (cd/m^2)
High voltage treatment applied (55a, 53b)	12	300
High voltage treatment not applied (55b-55c, 53a)	<0.05	0

(Example 3)

An organic EL device having a sectional structure as shown in Figure 3 (before formation of a different conductivity region 53b) was prepared in the

same manner as in Example 2 except for using HPOT
(hexabis(pentyloxy)triphenylene) of a formula shown
below was used instead of HHOT for providing a
conductive liquid crystal layer 53.

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HPOT $R = C_5H_{11}O$

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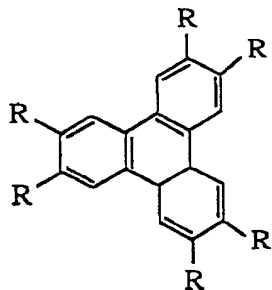
After the above device preparation, a portion
of the conductive liquid crystal layer 53

15 (corresponding to a luminescence segment 55a in Figure
3) was irradiated with GaAlAs laser beam (beam
diameter = ca. 20 μm, 10 mW) similarly as in Example 1
to form a different conductivity region (53b shown in
Figure 3).

20 Thereafter, the device was subjected to
application of an electric field of 12 volts/100 nm,
whereby the irradiated part and non-irradiated parts
exhibited different luminances as shown in Table 3
below.

25

Table 3

	Current (mA/cm^2)	Luminance (cd/m^2)
Laser-irradiated aligned parts (55a, 53b)	11.5	500
Non-irradiated non-aligned parts (55b-55c, 53a)	2.3	90

The same device exhibited luminance

differences at irradiated parts and non-irradiated

parts at an electric field of 10 volts/100 nm as shown

in Table 4 below.

Table 4

	Current (mA/cm^2)	Luminance (cd/m^2)
Laser-irradiated aligned parts (55a, 53b)	3.0	110
Non-irradiated non-aligned parts (55b-55c, 53a)	0.4	18

As described above, according to the present

invention, it has become possible to provide an

organic EL device having a memory characteristic by
including a conductive liquid crystal layer having
regions of different conductivities. Compared with a
conventional EL device lacking a recordability (memory

5   characteristic) of written or display state, the EL
device of the present invention can exhibit locally
different luminances at an identical drive voltage.
This characteristic is available not only in a display
device, but also in a memory device.

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